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- (74) Agents: WAIN, Christopher, Paul et al.; A.A. Thornton & Co., 235 High Holborn, London WC1V 7LB (GB).
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- (71) Applicant (for all designated States except US): HAL-LIBURTON ENERGY SERVICES, INC. [US/US]; P.O. Box 1431, Duncan, OK 73533 (US).
- (71) Applicant (for MW only): WAIN, Christopher, Paul [GB/GB]; A.A. Thornton & Co., 235 High Holborn, London WC1V 7LB (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): NGUYEN, Philip, D. [US/US]; 1107 Jones Avenue, Duncan, OK 73533 (US). BARTON, Johnny, A. [US/US]; 1002 N 2nd Street, Marlow, OK 73055 (US). ISENBERG, O., Marlene [US/US]; 1290 Woodside, Duncan, OK 73533 (US).
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(54) Title: RESIN COMPOSITIONS AND METHODS OF USING RESIN COMPOSITIONS TO CONTROL PROPPANT FLOW-BACK

(57) Abstract: The present invention described a resin composition comprising from about 5 % to about 30 % phenol, from about 40 % to about 70 % phenol formaldehyde, from about 10 % to about 40 % furfuryl alcohol, from about 0.1 % to about 3 % of a silane coupling agent, and from about 1 % to about 15 % of a surfactant and methods of using of that resin in controlling particulate flowback from a subterranean formation.

WO 2005/080749 A2

## RESIN COMPOSITIONS AND METHODS OF USING RESIN COMPOSITIONS TO CONTROL PROPPANT FLOW-BACK

### Background of the Invention

#### 1. Field of the Invention.

The present invention relates to enhancing the conductivity of subterranean formations while controlling proppant flowback. More particularly, the present invention relates to improved resin compositions and resin-coated proppants and their use in controlling proppant flowback.

#### 2. Description of Related Art.

Hydrocarbon-producing wells are often stimulated by hydraulic fracturing treatments. In hydraulic fracturing treatments, a viscous fracturing fluid, which also functions as a carrier fluid, is pumped into a producing zone to be fractured at a rate and pressure such that one or more fractures are formed in the zone. Particulate solids for propping the fractures, commonly referred to in the art as "proppant," are generally suspended in at least a portion of the fracturing fluid so that the particulate solids are deposited in the fractures when the fracturing fluid reverts to a thin fluid to be returned to the surface. The proppant deposited in the fractures functions to prevent the fractures from fully closing and maintains conductive channels through which produced hydrocarbons can flow.

In order to prevent the subsequent flowback of proppant and other unconsolidated particulates with the produced fluids a portion of the proppant introduced into the fractures may be coated with a hardenable resin composition. When the fracturing fluid, which is the carrier fluid for the proppant, reverts to a thin fluid the resin-coated proppant is deposited in the fracture, and the fracture closes on the proppant. Such partially closed fractures apply pressure on the resin-coated proppant particles, causing the particles to be forced into contact with each other while the resin composition hardens. The hardening of the resin composition under pressure brings about the consolidation of the resin-coated proppant particles into a hard permeable mass having compressive and tensile strength that hopefully prevents unconsolidated proppant and formation sand from flowing out of the fractures with produced fluids. Flowback of the proppant or formation fines with formation fluids is undesirable as it may erode metal equipment, plug piping and vessels, and cause damage to valves, instruments, and other production equipment.

Using heretofore known hardenable resin compositions has been disadvantageous because they have short shelf lives. That is, the shelf lives of the hardenable resin components, once mixed, have heretofore been as short as about four hours or less. It has been a common practice to utilize proppant that is pre-coated with a resin composition. However, such pre-coated resins generally begin to cure immediately after they are mixed and coated onto the proppant so that by the time the proppant is used, the resin may be more than 90% cured. When such pre-cured resin completes curing once placed in the subterranean formation, the resulting consolidated proppant pack often does not have enough strength to prevent deterioration of the proppant pack and proppant flowback.

### **SUMMARY OF THE INVENTION**

The present invention relates to enhancing the conductivity of subterranean formations while controlling proppant flowback. More particularly, the present invention relates to improved resin compositions and resin-coated proppants and their use in controlling proppant flowback.

One embodiment of the present invention provides a resin composition comprising from about 5% to about 30% phenol, from about 40% to about 70% phenol formaldehyde, from about 10 to about 40% furfuryl alcohol, from about 0.1% to about 3% of a silane coupling agent, and from about 1% to about 15% of a surfactant.

Another embodiment of the present invention describes a method of controlling proppant flowback from a fracture in a subterranean zone comprising the steps of coating the resin as described above onto at least a portion of provided proppant particles, introducing those resin-coated proppant particles into a subterranean fracture, and allowing the resin on the resin-coated proppant to substantially cure.

The objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments that follows.

### **DESCRIPTION OF PREFERRED EMBODIMENTS**

The present invention provides improved resin compositions and proppants coated with such improved resin compositions suitable for use in enhancing the conductivity of subterranean formations while controlling proppant flowback.

When the resin composition of the present invention is used to coat proppant particles in a subterranean fracturing operation, any fracturing fluid known in the art may be used,

including aqueous gels, emulsions, and other suitable fracturing fluids. The aqueous gels are generally comprised of water and one or more gelling agents. The emulsions may be comprised of two or more immiscible liquids such as an aqueous gelled liquid and a liquefied, normally gaseous fluid, such as nitrogen. The preferred fracturing fluids for use in accordance with this invention are aqueous gels comprised of water, a gelling agent for gelling the water and increasing its viscosity, and optionally, a cross-linking agent for cross-linking the gel and further increasing the viscosity of the fluid. The increased viscosity of the gelled or gelled and cross-linked fracturing fluid, *inter alia*, reduces fluid loss and allows the fracturing fluid to transport significant quantities of suspended proppant particles. The fracturing fluids may also include one or more of a variety of well-known additives such as breakers, stabilizers, fluid loss control additives, clay stabilizers, bactericides, and the like.

The water utilized in the fracturing fluid may be fresh water, salt water (*e.g.*, water containing one or more salts dissolved therein), brine (*e.g.*, saturated salt water), or seawater. Generally, the water can be from any source provided that it does not contain an excess of compounds that adversely affect other components in the resin composition or the performance of the resin composition relative to the subterranean conditions to which it may be subjected.

Proppant particles utilized in accordance with the present invention are generally of a size such that formation particulates that may migrate with produced fluids are prevented from being produced from the subterranean zone. Any suitable proppant may be utilized, including graded sand, bauxite, ceramic materials, glass materials, walnut hulls, polymer beads and the like. Generally, the proppant particles have a size in the range of from about 2 to about 400 mesh, U.S. sieve series. In some embodiments of the present invention, the proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. Particle size distribution ranges are generally one or more of 10-20 mesh, 20-40 mesh, 40-60 mesh or 50-70 mesh, depending on the particular size and distribution of formation particulates to be screened out by the consolidated proppant particles.

The improved resin compositions of the present invention comprise phenol, phenol formaldehyde, furfuryl alcohol, a silane coupling agent, and a surfactant. The resin compositions of the present invention may be useful in a variety of subterranean conditions but are particularly well suited for use in subterranean formations exhibiting temperatures above about 200°F. The resins of the present invention do not begin to cure until they are

exposed to temperatures above about 175°F. Thus, the resins of the present invention can be prepared and then stored for long periods of time at temperatures below about 175°F without concern that the resin compositions will become unusable over time.

Phenol is a commercially available, hydroxy benzene derivative, aromatic alcohol that exhibits weak acidic properties and contains a hydroxyl group attached to a benzene ring. The resins of the present invention comprise from about 5% to about 30% phenol by weight of the overall resin composition.

Phenol formaldehyde is a commercially available synthetic polymer made from phenol and formaldehyde monomers. The resins of the present invention comprise from about 40% to about 70% phenol formaldehyde by weight of the overall resin composition.

Furfuryl alcohol is a primary alcohol and an oligomer of furan resin that is colorless or pale yellow in appearance. In the resins of the present invention, the furfuryl alcohol polymerizes from an oligomer form into a stable furan resin polymer. The resins of the present invention comprise from about 10% to about 40% furfuryl alcohol by weight of the overall resin composition.

Silane coupling agents are chemicals that contain silicone at the center of the silane molecule that is chemically attached to a first functional group such as vinyl, amino, chloro, epoxy, mercapto, and a second functional group such as methoxy or ethoxy. Silane coupling agents act such that the first functional group may attach to an organic compound while the second functional group may attach to an inorganic material or substrate to achieve a "coupling" effect. Any silane coupling agent that is compatible with the hardening agent and facilitates the coupling of the resin to the surface of the formation sand particles is suitable for use in the present invention. Examples of preferred silane coupling agents suitable for use in the present invention include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypopyltrimethoxysilane, n-beta- (aminoethyl)-gamma-aminopropyl trimethoxysilane, and combinations thereof. The silane coupling agent used is included in the resin in an amount capable of sufficiently bonding the resin to the particulate. In some embodiments of the present invention, the silane coupling agent used is included in the liquid hardenable resin component in the range of from about 0.1% to about 3% by weight of the liquid hardening agent component.

Any surfactant compatible with the other components of the resin composition may be used in the present invention. Such surfactants include, but are not limited to, an ethoxylated

nonyl phenol phosphate ester, mixtures of one or more cationic surfactants, and one or more non-ionic surfactants and an alkyl phosphonate surfactant. The mixtures of one or more cationic and nonionic surfactants are described in U.S. Patent No. 6,311,773, issued to Todd et al. on November 6, 2001, which is incorporated herein by reference. A  $C_{12} - C_{22}$  alkyl phosphonate surfactant is preferred. The surfactant or surfactants utilized are included in the liquid hardening agent component in an amount in the range of from about 1% to about 15% by weight of the liquid hardening agent component.

Any solvent that is compatible with the hardenable resin and achieves the desired viscosity effect is suitable for use in the present invention. Preferred solvents are those having high flash points (most preferably about 125°F). As described above, use of a solvent in the hardenable resin composition is optional but may be desirable to reduce the viscosity of the hardenable resin component for a variety of reasons including ease of handling, mixing, and transferring. It is within the ability of one skilled in the art, with the benefit of this disclosure, to determine if and how much solvent is needed to achieve a suitable viscosity. Solvents suitable for use in the present invention include, but are not limited to, 2-butoxy ethanol, butylglycidyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl sulfoxide, dimethyl formamide, diethyleneglycol methyl ether, diethylene glycol dimethyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, gamma-butyrolactone, butylene carbonate, propylene carbonate, ethylene carbonate, methanol, butyl alcohol, d'limonene, fatty acid methyl esters, and combinations thereof.

The amount of resin of the present invention coated onto the proppant particles generally ranges from about 0.1% to about 10% by weight of the proppant. When it is desirable or necessary to conserve a major portion of the resin composition, the resin composition may be applied to an initial portion of the proppant particles, not applied or intermittently applied to the middle portion of the proppant particles, and applied to the last portion of the proppant particles deposited in the fractures. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate combination to achieve the desired conservation goals, consolidation, and permeability goals.

In one embodiment of the methods of the present invention, a resin composition is created as described above that is then coated onto proppant particles to form resin-coated proppant particles that are subsequently mixed with a viscous fracturing fluid. The viscous fracturing fluid containing resin-coated proppant particles is then introduced into a

subterranean zone having one or more fractures therein and the resin-coated proppant particles are placed in at least one fracture. The resin-coated proppant particles are then allowed to harden and consolidate into one or more high-strength permeable packs that prevent proppant flowback.

To facilitate a better understanding of the present invention, the following examples of some of the preferred embodiments are given. In no way should such examples be read to limit the scope of the invention.

## EXAMPLES

### Example 1

A resin of the present invention was prepared by mixing 0.75 mL of phenol, 6.1 mL of phenol formaldehyde, 2.55 mL of furfuryl alcohol, 0.1 mL of silane coupling agent n-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, and 0.5 mL of an alkyl phosphonate surfactant. A volume of 7.5 mL of the resin mixture was then coated onto 250 grams of 20/40-mesh bauxite proppant. The coated proppant was then mixed with 300 mL of a fracturing fluid using carboxymethylhydroxypropyl guar as the gelling base. That gelled fluid was cross-linked with a zirconium cross-linker. The resulting viscous fracturing fluid comprising resin-coated proppant was stirred in a heated bath for 1 hour at 175°F before being packed in brass flow cells. No closure stress was exerted on the cells and they were allowed to cure in an oven at various temperatures and for various lengths of time. Consolidated cores were obtained from the proppant packs to determine the unconsolidated compressive strength (UCS). The results of these tests are illustrated in Table 1, below:

Table 1: Effect of Cure Temperature and Cure Time on Unconfined Compressive Strength (psi) of Resin-Treated Proppant

Cure Time	Cure Temperature				
	225°F	250°F	275°F	300°F	325°F
2 hrs	12	16	113	540	489
3 hrs	101	96	392	654	580
6 hrs	195	314	590	593	779
24 hrs	---	---	---	---	765
96 hrs	---	---	---	---	860

The results in Table 1 illustrate that the resin compositions of the present invention, when allowed to cure at temperatures greater than or equal to 175, quickly yield compressive strengths suitable for use in subterranean applications.

### Example 2

A modified API conductivity flow cell was used to perform proppant flowback testing to determine the effectiveness of the resin of the present invention in controlling proppant flowback. The conductivity flow cell was modified in that a 0.5-inch hole was installed at one end of the flow cell to simulate a perforation and a wire-mesh screen was initially inserted in the perforation to prevent production of the proppant. Ceramic proppant of 20/40-mesh was coated with 3% resin by weight of the proppant. The resin composition used was identical to that described in Example 1. The resin-coated proppant was then slurried into a viscous fracturing fluid as described in Example 1. The proppant slurry was packed into the modified conductivity cell to a loading of 2 lb/ft<sup>2</sup> and set at an initial closure stress of 2,000 psi and a temperature of 150°F. After 2 hours, the temperature of the cell was increased to 300°F and after 6 hours the closure stress was increased to 6,000 psi. The cell was allowed to set at 300°F and 6,000 psi for 12 additional hours after which a flowing dry gas was fed through the cell at 50 standard liters per minute and an internal pressure of 400 psi. Following the treatment with the dry gas, the internal pressure on the cell was released, the wire-mesh screen was removed from the perforation, and dry gas was again fed to the cell. The gas was allowed to exit through the perforation and proppant production was monitored. Even once the dry gas feed rate increased to 760 standard liters per minute (which is equivalent to a field, gas production flow rate of 155 MMSCFT per day), only a few grains of proppant exited the cell, illustrating that the resin compositions of the present invention are capable of consolidating particulates and controlling proppant flowback.

Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.



What is claimed is:

1. A method of controlling proppant flowback from a fracture in a subterranean zone comprising the steps of:

providing a resin composition comprising:

from about 5% to about 30% phenol;

from about 40% to about 70% phenol formaldehyde;

from about 10 to about 40% furfuryl alcohol;

from about 0.1% to about 3% of a silane coupling agent; and,

from about 1% to about 15% of a surfactant;

providing proppant particles;

coating the resin composition onto at least a portion of the proppant particles to create resin-coated proppant particles;

introducing the resin-coated proppant particles into the subterranean fracture; and,

allowing the resin on the resin-coated proppant to substantially cure.

2. The method of claim 1 wherein the silane coupling agent is N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, n-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, or combinations thereof.

3. The method of claim 1 wherein the surfactant comprises ethoxylated nonyl phenol phosphate ester, a cationic surfactant, a non-ionic surfactant, an alkyl phosphonate surfactant, or combinations thereof.

4. The method of claim 1 wherein the amount of resin composition coated onto the proppant is from about 0.1% to about 5% by weight of the proppant.

5. The method of claim 1 wherein the resin further comprises a solvent.

6. The method of claim 5 wherein the solvent comprises 2-butoxy ethanol, butylglycidyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl sulfoxide, dimethyl formamide, diethyleneglycol methyl ether, diethylene glycol dimethyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, gamma-butyrolactone, butylene carbonate, propylene carbonate, ethylene carbonate, methanol, butyl alcohol, d'limonene, fatty acid methyl esters, or combinations thereof.

7. A resin composition comprising:

from about 5% to about 30% phenol;

from about 40% to about 70% phenol formaldehyde;  
from about 10 to about 40% furfuryl alcohol;  
from about 0.1% to about 3% of a silane coupling agent; and,  
from about 1% to about 15% of a surfactant.

8. The resin of claim 7 wherein the silane coupling agent is N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, n-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, or combinations thereof.

9. The resin of claim 7 wherein the surfactant is ethoxylated nonyl phenol phosphate ester, a cationic surfactant, a non-ionic surfactant, an alkyl phosphonate surfactant, or combinations thereof.

10. The resin of claim 7 further comprising a solvent.

11. The resin of claim 10 wherein the solvent comprises 2-butoxy ethanol, butylglycidyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl sulfoxide, dimethyl formamide, diethyleneglycol methyl ether, diethylene glycol dimethyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, gamma-butyrolactone, butylene carbonate, propylene carbonate, ethylene carbonate, methanol, butyl alcohol, d'limonene, fatty acid methyl esters, or combinations thereof.

12. A proppant coated with a resin composition wherein the resin composition comprises:

from about 5% to about 30% phenol;  
from about 40% to about 70% phenol formaldehyde;  
from about 10 to about 40% furfuryl alcohol;  
from about 0.1% to about 3% of a silane coupling agent; and,  
from about 1% to about 15% of a surfactant.

13. The resin-coated proppant of claim 12 wherein the silane coupling agent is N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, n-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane, or combinations thereof.

14. The resin-coated proppant of claim 12 wherein the surfactant is ethoxylated nonyl phenol phosphate ester, a cationic surfactant, a non-ionic surfactant, an alkyl phosphonate surfactant, or combinations thereof.

15. The resin-coated proppant of claim 12 wherein the amount of resin coated onto the proppant is from about 0.1% to about 5% by weight of the proppant.

16. The resin-coated proppant of claim 12 wherein the resin further comprises a solvent.

17. The resin-coated proppant of claim 16 wherein the solvent comprises 2-butoxy ethanol, butylglycidyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl sulfoxide, dimethyl formamide, diethyleneglycol methyl ether, diethylene glycol dimethyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, gamma-butyrolactone, butylene carbonate, propylene carbonate, ethylene carbonate, methanol, butyl alcohol, d'limonene, fatty acid methyl esters, or combinations thereof.